



Massive Ti^{3+} self-doped by the injected electrons from external Pt and the efficient photocatalytic hydrogen production under visible-light



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ABSTRACT

Ti^{3+} doping in TiO_2 photocatalyst has attracted much attention due to its enhanced visible-light absorption and the decreased carrier recombination. However, the introduction of massive stable Ti^{3+} is still a great challenge because Ti^{3+} is easy to be oxidized in air. In this work, for the first time, a negatively charged core/shell TiO_2/C nanostructure is prepared and then Pt^0 atoms reduced by NaBH_4 are loaded on its surface. Through a tracking test of the product's Zeta potential, XPS and FTIR measurements, it is found that the reductive electrons are produced due to the reaction between C and metal Pt, in which Pt exhibits a +2 chemical valence. And the lost electrons by Pt are transferred into the interior TiO_2 through the carbon shell and reduce Ti^{4+} to Ti^{3+} . This method avoids Ti^{3+} ions' exposing to air and overcomes the complex coating process for isolating oxygen, and provides a new facile one for efficiently Ti^{3+} self-doping. Through the following measurements, such as XPS, PL, EPR and Raman etc., it is proved that massive Ti^{3+} ions are formed in the interior TiO_2 , which greatly narrows the composite's band-gap (from 3.11 eV to 2.47 eV) and enhances the visible-light absorption. As a result, the as-obtained sample exhibits a larger carrier densities ($13.9 \times 10^{18} \text{ cm}^{-3}$) and a higher photocatalytic activity under visible-light irradiation compared with those in other literatures: the rate of photocatalytic water splitting for H_2 generation is up to $8117 \mu\text{mol h}^{-1} \text{ g}^{-1}$.

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1. Introduction

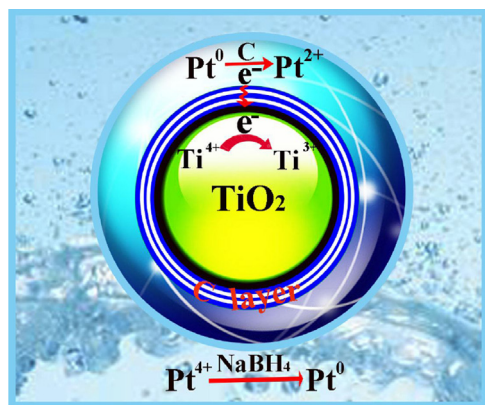
Ti^{3+} doping has been extensively studied in the TiO_2 based materials for photocatalytic hydrogen generation, solar cells, waste water purification, and solar thermal collectors etc. [1–5]. The doping brings several outstanding benefits, such as narrowing the band gap [1], enhancing effective visible-light absorption [3] and reducing carrier recombination centers [4]. However, it is also found that the low quantity of Ti^{3+} in TiO_2 leads to the production of localized oxygen vacancy states under the conduction band minimum of TiO_2 , which damages the flow of electrons and thus lowers the

photocatalytic activity [6,7]. Conversely, the high concentration of Ti^{3+} in TiO_2 promotes the flow of electrons and enhances the photocatalytic activity [8–10]. It is also noted that Ti^{3+} is extremely unstable in the air and can be rapidly oxidized, which often results in a small quantity of Ti^{3+} self-doping in many previous works [11–14]. So the realization of an abundant and stable Ti^{3+} doping in TiO_2 through a facile method is still a big challenge. So far, a series of studies have been attempted to dope a large number of stable Ti^{3+} in TiO_2 by some man-made strategies, such as hydrogenation [15,16], high energy particle bombardment (laser, electron or Ar^+) [17–19], redox with reducing agents (Zn, Al, DEG, NaBH_4 , CO) [12,20–23], photochemical synthesis [24,25], and partial oxidation of Ti based low valent compounds (TiH_2 , TiO , Ti_2O_3 and TiCl_3) [26–28]. However, all the above strategies have their own shortages, such as complex experimental process, high-price cost, expensive agents, especially low doping quantity and weak stability. These problems promote many researchers to explore a new method for efficiently Ti^{3+} self-doping.

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Scheme 1. The formation mechanism of Ti^{3+} in TiO_2 .

In this work, as shown in Scheme 1, it is found by us that the reductive electrons are produced due to the formation of a Pt-C bond between C in the negatively charged TiO_2/C sample and metal Pt, in which Pt exhibits a +2 chemical valence. Then the electrons are easily transferred into the interior TiO_2 through the outside carbon shell then reduce Ti^{4+} to Ti^{3+} , in which the as-coated carbon is used as a shield for protecting Ti^{3+} from oxidation. The measurement results prove that a large number of stable Ti^{3+} are formed in the carbon-coated TiO_2 after this simple chemical treatment. And the as-obtained sample exhibits a high catalytic activity (up to $8117 \mu\text{mol h}^{-1} \text{g}^{-1}$) for hydrogen generation through water splitting under visible-light and a large carrier densities ($13.9 \times 10^{18} \text{ cm}^{-3}$). This rate of photocatalytic for H_2 generation is around 16 times of that of the sample without Ti^{3+} doping ($507 \mu\text{mol h}^{-1} \text{g}^{-1}$).

2. Experimental section

2.1. Preparation of TiO_2 nanorods

All the chemicals were of analytical grade. TiO_2 nanorods were synthesized according to the literature [29] using an alkaline hydrothermal process.

2.2. Preparation of TiO_2/C NTs

TiO_2/C nanorods were prepared by a vacuum infiltration process. In a typical procedure, 0.1 g glucose was first stirred in deionized water (40 mL) under high purity nitrogen gas for 1 h. Then 1 g TiO_2 nanorods were added into the above solution under argon atmosphere and stirred for 4 h. Finally, the resulting sample was carbonized at 400°C for 2 h under argon atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$.

2.3. Preparation of Ti^{3+} doped TiO_2/C nanorods

Ti^{3+} doped TiO_2/C nanorods have been synthesized by a simple chemical reduction method, which were named as $\text{Ti}^{3+}/\text{TCP}$. In a typical procedure, TiO_2/C nanorods (1 g) were dispersed in a H_2PtCl_6 aqueous solution (0.005 M, 40 mL), and vigorously agitated for 2 h. Then 0.1 M NaBH_4 cold aqueous solution was dropwise added in it and stirred for 4 h. The molar ratio of Pt to NaBH_4 is 1:10. Finally, the resultant sample was collected by centrifuged and washed with distilled water and ethanol, dried in a vacuum furnace at 60°C for 24 h. TiO_2/Pt sample was prepared by the same chemical reduction method, in which TiO_2 was used as precursor. And $\text{Ti}^{3+}/\text{TCP-F}$ was prepared through a similar procedure, only adding few H_2PtCl_6 aqueous solution (0.005 M, 25 mL).

2.4. Preparation of $\text{TiO}_2/\text{C}/\text{Pt}$ nanorods

$\text{TiO}_2/\text{C}/\text{Pt}$ nanorods were prepared by a mechanical mixing of TiO_2/C nanorods with Pt nanoparticles (0.2 mM) reduced by the similar reduction method.

3. Results and discussions

3.1. Structures and compositions

The chemical composition and valence state of the elements in the $\text{Ti}^{3+}/\text{TCP}$ composite are firstly analyzed by X-ray photoelectron spectroscopy (XPS) measurements. Fig. 1a show the Ti 2p of the $\text{Ti}^{3+}/\text{TCP}$ sample. Compared to the Ti 2p XPS spectra (Fig. S3a) of the TiO_2/C sample, there are two additional peaks at 457.6 (Ti $2p_{3/2}$) and 463.2 eV (Ti $2p_{1/2}$), which are typical characteristic peaks of the Ti^{3+} .¹² In addition, the other two peaks centered at 458.7 and 464.5 eV, which are consistent with Ti^{4+} in TiO_2 lattice [30]. The quantitative analysis of XPS results illustrates that abundant Ti^{3+} and Ti^{4+} are coexisted in the $\text{Ti}^{3+}/\text{TCP}$ sample. Fig. 1b show the O 1s spectra of the $\text{Ti}^{3+}/\text{TCP}$ sample. Obviously, it can be seen that there are two peaks, the peak at 529.2 eV is assigned to $\text{Ti}^{4+}-\text{O}$, and the other peak at 530.2 eV is assigned to $\text{Ti}^{3+}-\text{O}$ or $-\text{OH}$ in the $\text{Ti}^{3+}/\text{TCP}$ sample [8,14]. Fig. 1c shows the C 1s XPS spectra of the $\text{Ti}^{3+}/\text{TCP}$ sample. The peak around 284.6 and 288.6 eV are attributed to $\text{C}=\text{C}$ bond and $\text{C}=\text{O}$ bond, respectively [31,32]. Interestingly, after NaBH_4 reducing, not all the Pt atoms are Pt^{4+} and Pt^0 . As shown in Fig. 1d, the $4f_{7/2}$ and $4f_{5/2}$ characteristic peaks of Pt^0 are observed at 71.3 and 74.9 eV [33], respectively. And the peaks attributed to the $4f_{7/2}$ and $4f_{5/2}$ of Pt^{2+} are also found at 72.2 and 75.8 eV [33], respectively. Furthermore, the two peaks at 74.2 and 77.3 eV are derived from the $4f_{7/2}$ and $4f_{5/2}$ of Pt^{4+} [33].

X-ray diffraction (XRD) analysis is further conducted to characterize the compositions of raw TiO_2 and TiO_2/C , $\text{Ti}^{3+}/\text{TCP}$ sample. As shown in Fig. 2a, peaks appeared in the TiO_2 , TiO_2/C , $\text{Ti}^{3+}/\text{TCP}$ nanorods can be well indexed to an anatase phased TiO_2 (JCPDS No. 21-1272). No diffraction peak of C are observed because of its little amount. And no obvious shift of the TiO_2 diffraction peaks and lattice deformation are found. In order to further demonstrate the presence of Ti^{3+} , electron para-magnetic resonance (EPR) and vibrating sample magnetometer (VSM) measurements are employed. As shown in Fig. 2b, a sharp and steep signal at $g = 1.98$ certainly indicates the massive existence of Ti^{3+} in the $\text{Ti}^{3+}/\text{TCP}$ sample [34]. EPR has also been carried out to detect the presence of Ti^{3+} in TiO_2 and TiO_2/C samples. As shown in Fig. S5, the EPR characteristic peak of Ti^{3+} isn't found, which further confirms the absence of Ti^{3+} in TiO_2 and TiO_2/C samples. In addition, the standard hysteresis loop of the $\text{Ti}^{3+}/\text{TCP}$ sample (Fig. S6) also clearly evidences the presence of Ti^{3+} . The $\text{Ti}^{3+}/\text{TCP}$ nanorods show a relatively stronger saturation magnetizations (M_s) of 0.02 emu/g compared to Ti^{3+} doped TiO_2 samples reduced by Al in the literature [1], which means that a large number of stable Ti^{3+} doping in TiO_2 . Raman spectroscopy is also conducted to affirm the atoms' status, as illustrated in Fig. 2c and Fig. S7. The spectra of TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ exhibit four same peaks at 143 cm^{-1} , 394 cm^{-1} , 512 cm^{-1} and 633 cm^{-1} respectively, attributed to the anatase TiO_2 [35]. In addition, the peak located at about 1360 cm^{-1} is the D peak of carbon, denoting to the edge distortion and structural disorder of carbon [30]. And the other peak at about 1590 cm^{-1} is the G peak of carbon associated with the graphitic carbon [30]. The G/D intensity ratio of $\text{Ti}^{3+}/\text{TCP}$ is 2.63, which is smaller than that of TiO_2/C (2.83), indicating that an increased disorder of the graphene structures after Pt loading. Meanwhile, compared with the Raman spectrum of TiO_2/C , the D and G peaks of the $\text{Ti}^{3+}/\text{TCP}$ sample show an obvious blue shift, indicating that a strong interaction between TiO_2

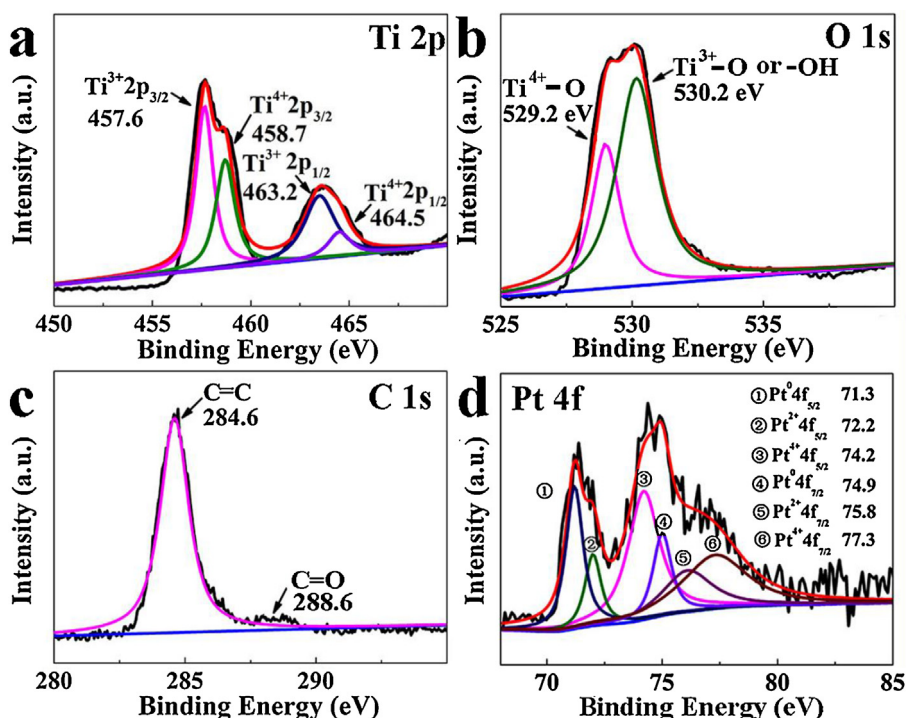


Fig. 1. XPS of Ti^{3+} /TCP sample. (a) Ti 2p spectra; (b) O 1s spectra; (c) C 1s spectra; (d) Pt 4f spectra.

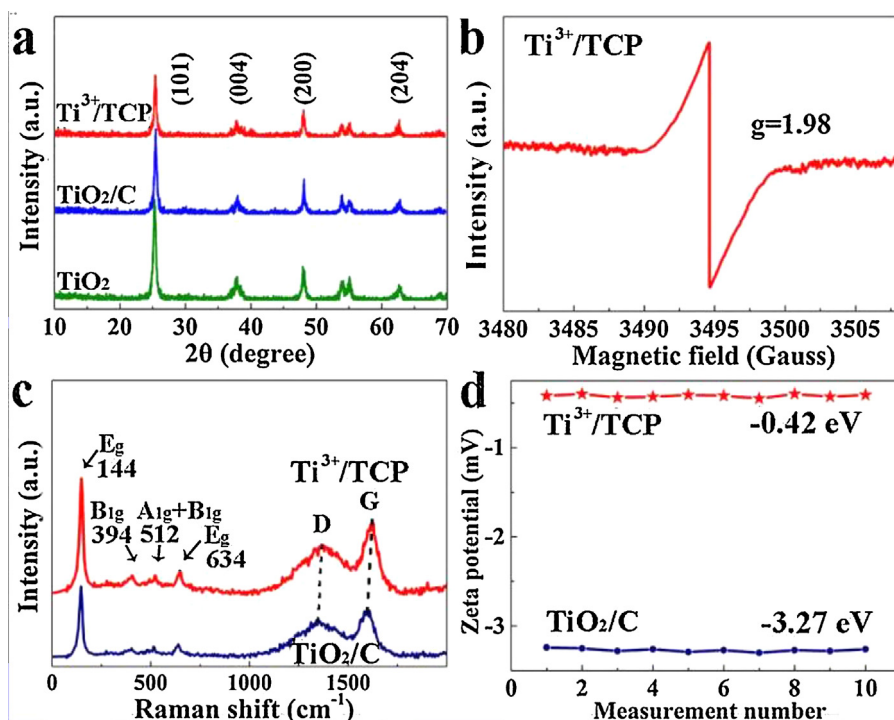


Fig. 2. (a) XRD patterns of the TiO_2 , TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ samples. (b) EPR spectra of the $\text{Ti}^{3+}/\text{TCP}$ sample. (c) Raman spectra of the TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ samples. (d) Zeta potential of the TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ samples.

and the carbon sheets after Pt loading. Zeta potentials of TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ nanorods are shown in Figs. 2 d and S8. The Zeta potential of the raw TiO_2/C nanorods is -3.27 eV. However, after Ti^{3+} doping and Pt loading, the Zeta potential increased to -0.42 eV. The greatly increased potential are mainly due to the presence of abundant Pt^{2+} and Pt^{4+} ions existed on the surface of the $\text{Ti}^{3+}/\text{TCP}$ sample.

Figs. 3 a and S9 shows the scanning electron microscopy (SEM) images of the $\text{Ti}^{3+}/\text{TCP}$, TiO_2 and TiO_2/C samples. Clearly, it can

be seen that the raw TiO_2 nanorods with rather smooth surfaces are around 17 nm in diameter and 400 nm in length. After carbon-coating and Pt loading respectively, the diameter of TiO_2 nanorods varies from 15 nm to 20 nm. The morphology and structure of the $\text{Ti}^{3+}/\text{TCP}$ sample are further characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Fig. 3b of its TEM images, it is clear to see that about 4 nm Pt nanoparticles are well dispersed on

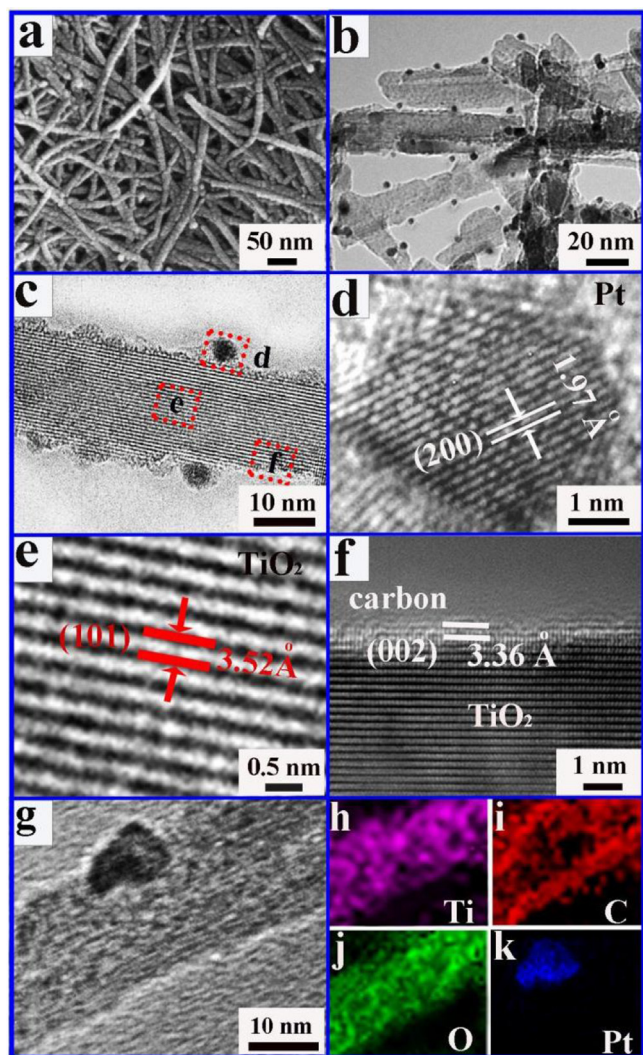


Fig. 3. SEM, TEM and HRTEM images of the $\text{Ti}^{3+}/\text{TCP}$ sample. (a) and (b) SEM and TEM images of the $\text{Ti}^{3+}/\text{TCP}$ nanorods; (c) HRTEM images of a typical nanorod; (d), (e) and (f) The enlarged HRTEM image of Pt section, TiO_2 section and the interface section; (g)–(k) TEM image of a typical $\text{Ti}^{3+}/\text{TCP}$ nanorod and its corresponding EDS element mappings of Ti, O, C and Pt elements.

every nanorod's surface, which roughen the nanorods and increase the sample's effective surface area. The following corresponding N_2 adsorption-desorption isotherm measurement results confirm the above presumption. As shown in Fig. S10, the surface areas of $\text{Ti}^{3+}/\text{TCP}$ and TiO_2/C samples are $159.01 \text{ m}^2 \text{ g}^{-1}$ and $149.22 \text{ m}^2 \text{ g}^{-1}$ respectively, which are greatly higher than that of TiO_2 precursor ($117.86 \text{ m}^2 \text{ g}^{-1}$). The HRTEM images of the framed areas in Fig. 3c–f show the lattice fringe spacings of 3.52, 3.36 and 1.97 Å, corresponding to the (101) plane of TiO_2 , (002) plane of graphitic carbon and (200) plane of Pt, respectively. In addition, the thickness of the carbon sheets is about 1.08 nm and consists of three carbon atom-layers, as shown in Fig. 3f. The TEM images and EDS mappings (Fig. 3g–k) also verify the composition of the sample: TiO_2 as a core, carbon sheet as a shell and Pt dispersed on the surface.

3.2. The conversion mechanism from Ti^{4+} to Ti^{3+}

As listed in the following equations of the oxidation-reduction potentials among Pt^0 , Pt^{2+} and Pt^{4+} ,



When Pt^{4+} is treated with a reductive agent, it will be transformed into Pt^0 quickly, which has been confirmed in many literatures [36–39]. So in this our work, for the first time, Pt^{4+} added in the system is reduced to Pt^0 by NaBH_4 , which is proved by a XPS measurement of the sample obtained by condensing the reaction solution. As shown in Fig. S11, only Pt^0 and Pt^{4+} are found in the sample, without Pt^{2+} . This means that Pt^{2+} subsequently appears after Pt^0 forming in the solution and landing on TiO_2/C . The formation of Pt^{2+} should be due to the reaction (Eq. (4)) between the negatively charged carbon (as indicated in Fig. 2d of the Zeta potential of TiO_2/C) and Pt^0 , which has also been found in recent works [33,40].



In this process, Pt–C chemical bonds are constructed. Their Raman results in Fig. 2c also testifies the changes induced by Pt–C bonds. As shown in Fig. 2c, the blue shifts of D and G peaks of carbon demonstrate that the stress induced by Pt–C bonds between Pt and carbon layers [41]. In order to further demonstrates the formation of Pt–C bonds, Fourier transform infrared (FTIR) measurements were conducted. As shown in Fig. S12, the peak at 458 cm^{-1} corresponds to the stretching vibration of O–Ti–O [42]. The C=C stretching vibration of the coated carbon layer at 1630 cm^{-1} is also found [43]. The signal at 3400 cm^{-1} is the characteristic peak of the surface –OH groups [44]. Notably, the peak appeared at 1092 cm^{-1} is assigned to the stretching vibration of Pt–C [45]. In addition, two peaks centered at 1469 cm^{-1} and 3030 cm^{-1} represent the C–H stretching vibration [46]. Obviously, a blue shift of the C–H stretching vibration peaks in the $\text{Ti}^{3+}/\text{TCP}$ sample is observed compared with that of $\text{TiO}_2/\text{C}/\text{Pt}$, which further proves the formation of Pt–C bonds [47]. Moreover, TG measurements in an air atmosphere further indicate the formation of Pt–C bonds. Fig. S13 shows the TG curves of $\text{TiO}_2/\text{C}/\text{Pt}$ and $\text{Ti}^{3+}/\text{TCP}$. Clearly, a same weight loss (2.5%) is found in two samples due to the combustion of carbon. However, the combustion temperature region of carbon in $\text{Ti}^{3+}/\text{TCP}$ ($25\text{--}513^\circ\text{C}$) is longer than that of $\text{TiO}_2/\text{C}/\text{Pt}$ ($25\text{--}424^\circ\text{C}$), indicating a higher thermal stability of $\text{Ti}^{3+}/\text{TCP}$. This can be ascribed to that the carbon layer is stabilized by the Pt nanoparticles due to the strong chemical coupling with the formation of Pt–C.

The redundant electrons lost by Pt^0 are transferred into the interior TiO_2 through the carbon layer and reduce Ti^{4+} to Ti^{3+} , as shown in Scheme 1 and the following equation:



In order to confirm that the reduction of Ti^{4+} in TiO_2 is induced by Pt, TiO_2/C sample is treated with a similar chemical reduction procedure, only without H_2PtCl_6 . As shown in Fig. S3c, no characteristic peak of the Ti^{3+} is detected. However, after adding a little H_2PtCl_6 aqueous solution (0.005 M, 25 mL), it is clear to see that the characteristic XPS peaks of Ti^{3+} are exhibited (Fig. 4a). The differences convincingly prove that the reduction of Ti^{4+} in TiO_2 is induced by Pt^0 . Notably, it is clearly observed that the content of Ti^{3+} in this sample (Fig. 4a) is less than that of $\text{Ti}^{3+}/\text{TCP}$ (Fig. 1a). It means that with the Pt content increasing, the Ti^{3+} content are obviously increased, which further confirms that the direct relation between the reduction of Ti^{4+} in TiO_2 and Pt addition.

3.3. Photocatalytic hydrogen production performance

Photocatalytic hydrogen production performance In this work, photoluminescence (PL) measurements is firstly used to evaluate the behavior of charges' separation and transport in the photocatalysts. As shown in Fig. 5a, the PL spectrum of $\text{Ti}^{3+}/\text{TCP}$ exhibits

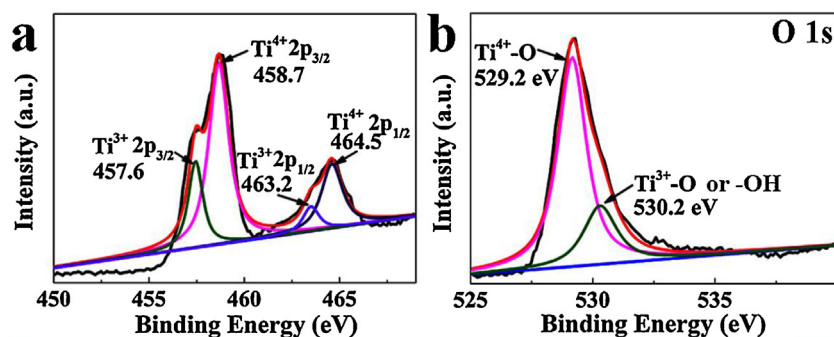


Fig. 4. The Ti 2p (a) and O 1s (b) XPS spectra of the $\text{Ti}^{3+}/\text{TCP}$ sample with a less addition of H_2PtCl_6 (0.005 M, 25 mL).

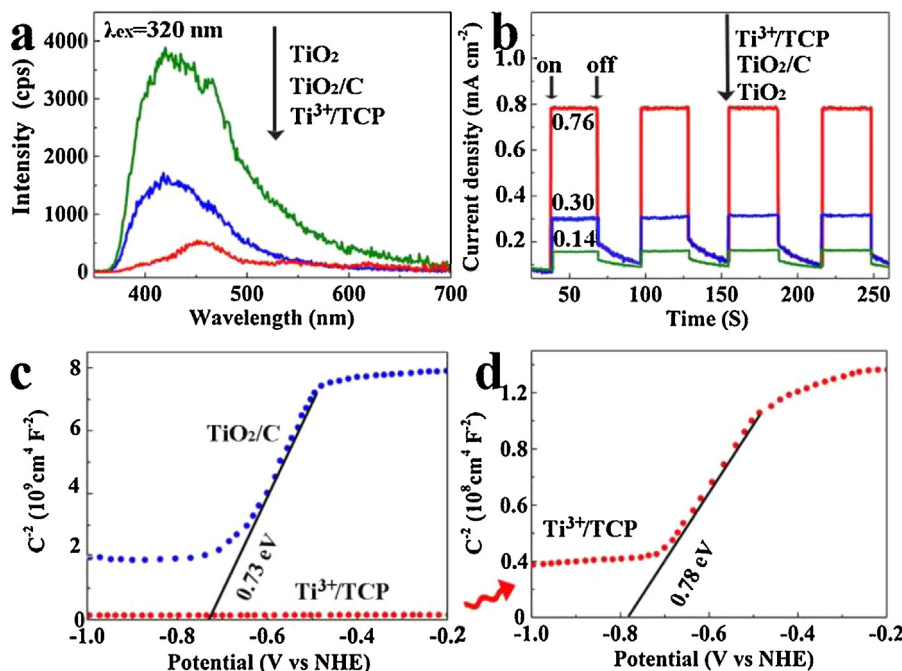


Fig. 5. (a) PL spectra of the TiO_2 , TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ samples; (b) Photocurrent densities of the TiO_2 , TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ samples; (c) and (d) Mott-Schottky plots of the TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ samples examined in the dark.

an extremely weak signal compared to those of TiO_2 and TiO_2/C , implying a lower recombination efficiency of excited electrons and holes [48]. This demonstrates that such a stable and abundant Ti^{3+} doping realizes a highly efficient separation of electron-hole pairs. Furthermore, the transient photocurrent responses of the samples with a same amount are tested under intermittent visible-light irradiation to further verify the separation effect. As shown in Fig. 5b, the transient photocurrent density of the $\text{Ti}^{3+}/\text{TCP}$ nanorods is 0.76 mA cm^{-2} , which is much higher than those of TiO_2 and TiO_2/C nanorods (TiO_2 : 0.14 mA cm^{-2} , TiO_2/C : 0.30 mA cm^{-2}). The remarkably improved photocurrent density indicates more electrons are produced and transferred in $\text{Ti}^{3+}/\text{TCP}$ due to the introduction of Ti^{3+} , which agrees with the PL measurement analysis. To further demonstrate the quick separation transport behaviors of charges in the $\text{Ti}^{3+}/\text{TCP}$ sample, electrochemical impedance spectra (EIS) is carried out in the dark and under visible-light irradiation, as shown in Fig. S16. Clearly, EIS spectrum of the sample both in the dark and under irradiation shows a semi-circle, indicating that it is charge transfer resistance limits the kinetics at the semiconductor interface [49–51]. Meanwhile, all the arc radii under irradiation are much smaller than those in the dark because of increased electron conductivity, which is well in accordance with those reported

in the previous literatures [52,53]. Notably, the $\text{Ti}^{3+}/\text{TCP}$ sample shows the smallest arc radius in all samples upon visible-light irradiation, suggesting a considerably effective charge separation and transport induced by the introduction of stable abundant Ti^{3+} . In addition, we measured the sample's carrier density through a Mott-Schottky method. As shown in Fig. 5c and d, the Mott-Schottky plots of TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$ nanorods show a positive slope, indicating that in these n-type semiconductors their Fermi level are about -0.73 eV and -0.78 eV (vs NHE) for TiO_2/C and $\text{Ti}^{3+}/\text{TCP}$, respectively. Moreover, according to the slopes of Mott-Schottky plots, carrier densities are calculated using the following equation [53]:

$$N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} \frac{d(1/C^2)}{dV} \quad (6)$$

where e_0 is the electronic charge, ε and ε_0 the dielectric constant of TiO_2 and the permittivity of vacuum, respectively, N_d is the carrier density, C is interfacial capacitance, and V is the applied voltage. In contrast, the carrier density of $\text{Ti}^{3+}/\text{TCP}$ ($13.9 \times 10^{18} \text{ cm}^{-3}$) is almost elevated to 10 times compared with that of TiO_2/C (1.42×10^{18}). It verifies that the introduction of abundant Ti^{3+} remarkably accelerates carrier's transfer, which well agrees with their photocurrent response results.

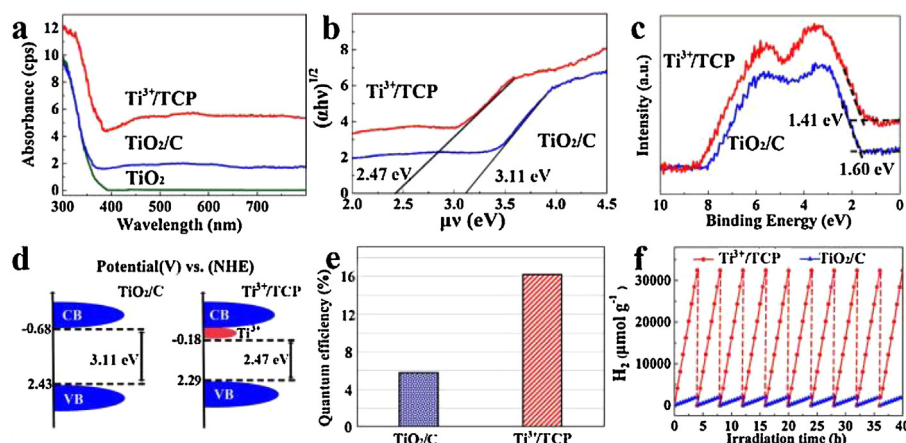


Fig. 6. (a) UV-vis DRS of the TiO₂, TiO₂/C and Ti³⁺/TCP samples. (b) Optical band gaps determined by the UV-vis DRS. (c) Valence-band spectra measured by XPS. (d) The band structures of the TiO₂/C and Ti³⁺/TCP nanorods. (e) The quantum efficiency of TiO₂/C and Ti³⁺/TCP nanorods. (f) Visible-light driven photocatalytic water splitting for H₂ generation in 10 repeated cycles (4 h/cycle).

Furthermore, the band gaps of the samples are analyzed by ultraviolet–visible diffuse reflectance spectrum (UV-vis DRS), as shown in Fig. 6a. Obviously, as shown in Fig. 6a, the visible-light absorption of TiO₂ nanorods is obviously enhanced after carbon coating. This is also proved by their color change from white to gray, as shown in Fig. S2. Notably, compared to that of TiO₂/C, the visible-light absorption intensity of Ti³⁺/TCP is greatly increased because of the narrowed band gap induced by abundant Ti³⁺ doping. Additionally, as a protective shield, carbon shell isolates the outside oxygen and strengthens the stability of Ti³⁺. In order to gain deeper insight into the change of energy band structures, according to the plots of the transformed Kubelka-Munk function of UV-vis DRS (Fig. 6b), the band gaps of TiO₂/C, Ti³⁺/TCP are characterized as 3.11 eV and 2.47 eV, respectively. The energy band structures of TiO₂/C and Ti³⁺/TCP are further ascertained by valence band (VB) XPS measurements, as shown in Fig. 6c. Apparently, the VB top of 1.60 and 1.41 eV below the Fermi level (E_F) are seen for TiO₂/C and Ti³⁺/TCP, respectively. The valence band values of TiO₂/C and Ti³⁺/TCP are 2.43 eV and 2.29 eV versus normal hydrogen electrode after a calibration with reference Fermi level, respectively. Compared with TiO₂/C, the valence band top of Ti³⁺/TCP shifts upward 0.14 eV and its conduction band shifts downward 0.50 eV, which originate from the introduction of abundant Ti³⁺. Based on the above results, the energy band structures of TiO₂/C and Ti³⁺/TCP nanorods are depicted in Fig. 6d. As shown in Fig. 6e and f, the TiO₂/C sample show good quantum efficiency (5.8%) and photocatalytic hydrogen production performance (507 $\mu\text{mol h}^{-1} \text{g}^{-1}$) under visible-light irradiation. Apart from the enhanced visible-light absorption, the improved photocatalytic performance is also attributed to the greatly enhanced electrical conductivity of TiO₂ induced by the carbon layers, leading to a rapid transportation and separation of photon-generated electrons and holes [54]. Most importantly, the Ti³⁺/TCP sample shows a significantly high H₂ evolution rate of 8117 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and an excellent quantum efficiency up to 16.2% at 420 nm, which is much higher than those of TiO₂/C nanorods. Furthermore, the H₂ evolution rate is much higher than other similar composites reported in literatures (Table S1), though under a lower energy illustration in our work. Moreover, the Ti³⁺/TCP sample exhibits a good catalytic stability, which retains its high photocatalytic activity even after a 40 h cycle reaction.

4. Conclusions

In summary, a large number of stable Ti³⁺ doping in TiO₂ is realized through a facile Pt-induced chemical reduction method.

Through a serial of detailed measurements and analysis, it is demonstrated that Ti³⁺/TCP sample exhibits an enhanced visible-light absorption. Resultantly, its photocatalytic hydrogen generation under visible-light is greatly enhanced and maintains a good stability. This strategy open a new window for the construction of abundant and stable Ti³⁺-doped photocatalyst.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.07.014>.

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